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Evaluation and speciation of heavy metals in the soil of the Sub Urban Region of Southern India

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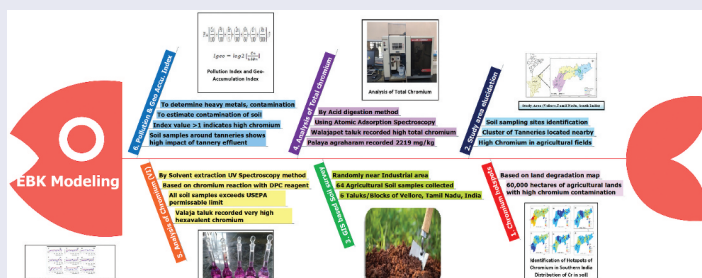
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ABSTRACT

This study examines the pollution of soil by chromium using statistical analysis and Empirical Bayesian Kriging (EBK) modeling around the leather tanning industries of Southern India. Sixty-four soil samples were collected from agricultural lands and analyzed for their major ions and trace elements using Atomic Absorption Spectrophotometer. It is observed that the concentration of trace elements, decreases in the following order: Cr > Fe > Ni > Pb > Mn > Cu > Zn. Also, the chromium present in the soil samples ranged between 0.1 and 2459 mg/kg. The higher concentration of Cr, Pb, Ni, and Zn observed in this study exceeds the permissible limit around tannery regions, indicating tannery effluents' impact. The positive correlation of Cr with Ca, Mg, Pb, and Mn specifies the discharge of tannery wastewater into the open land, thus contaminating the soil in the study area. The root mean square error (RMSE) values derived from the EBK model for Cr, Pb, Fe, and Ni are close to 1, indicating the model's validity. Moreover, the soil pollution index and Geo-accumulation index results around the tannery region show a profound impact of tannery effluent. The obtained results clearly emphasize the presence of toxic heavy metals in the study area that may cause extensive degradation of productive agricultural land. Hence, it is essential to make an appropriate strategy and implement a suitable remediation technique to solve the heavy metals pollution problem.

KEYWORDS

trace elements; chromium (III) and (VI); Pollution Index (PI); EBK modeling; Chromium speciation; Vellore District contamination



Introduction

Heavy metals' mobility and distribution are expounded not solely to their concentration but also their availability in the environment. Poor management and disposal of chromium (Cr) containing waste residue/ wastewater from industrial activities may cause environmental problems, leading to severe damage to the water, soil, and ecosystem (Chen et al. 2018). Indiscriminate tannery waste disposal has caused tough soil and water pollution in the Vellore and Dindigul districts of Tamil Nadu, where most tanneries exist. Soil and water pollution have drastically reduced crop yields in these areas and significantly decreased the total cropped area. Over the last two decades, the entire area under cultivation has decreased by 10.5% in Vellore and 41% in Dindigul. Usually, Cr is subjected to various chemical or biological transformations in contaminated soil and converted to a toxic form that is carcinogenic and mutagenic to humans and animals. It also attributes to slower plant growth and morphology changes (Nur-E-Alam et al. 2020).

An estimated 75000 tonnes of chromium are discharged into the atmosphere each year as an effect of human activities, and 54000 tons of chromium are further released to the environment by natural sources such as weathering and biochemical processes (WHO 1995). About 80% of Indian tanneries are engaged in the chrome tanning process, the most significant contributor to chromium pollution in India (Unceta et al. 2010). It is quantified that nearly 2000–3000 tonnes of chromium are released into the surroundings per year from tanneries in India alone (Ahamed and Kashif 2014). These industries consist of two types of tanning, such as vegetable and chrome tanning. The average wastewater discharges from chrome and vegetable tanneries are about 110 and 2400 Kl day⁻¹, respectively. Anthropogenic and natural sources contribute mixing of chromium with groundwater, surface water, and soil. The anthropogenic sources include contamination of water through many types of chromium (Cr) that are used in several industrial processes and manufacturing products such as chromium plating, leather tanning, electroplating, metal finishing, inhibition of metal corrosion, fabric paints and pigment manufactures, and application as catalyst (Kumar and Riyazuddin 2011; Laxmi and Kaushik 2020; Nirola et al. 2018; Tammamro et al. 2014).

Weathering of ultramafic rocks is a natural source of contamination and increases chromium concentration (Lilli et al. 2019). Dissolved Cr may result from rock-water interaction or industrial pollution. Chromium is commonly found in minerals such as garnets, amphiboles, spinels, micas, and pyroxenes (Zglinicki et al. 2020; Kanagaraj and Elango 2016). Many researchers have worked on chromium contamination in water (Kanagaraj and Elango 2019; Kumar 2014; Mondal and Singh 2011; Tariq et al. 2010; Venkatesan et al. 2021) and soils (Aceves et al. 2009; Avudainayagam et al. 2003; Barajas-Aceves, Corona-Hernández, and Rodríguez-Vázquez 2007; Bini, Maleci, and Romanin 2008; Cao et al. 2008; Gowd, Krishna, and Govil 2005; Gultekin et al. 2010; Hopp, Peiffer, and Durner 2006; Huang et al. 2009; Manoj, RamyaPriya, and Elango 2021; Moore, Attar, and Rastmanesh 2011; Shams et al. 2009; Stewart et al. 2003; Yang et al. 2019) around the tannery regions in the world.

The chemical reactivity, toxicity, and charge of chromium (Cr) in the soil can be found in two different oxidation states (Kamarudheen et al. 2020; Shi et al. 2020). Chromium in the environment occurs naturally in its trivalent and hexavalent forms.

Trivalent chromium (Cr-III) and hexavalent chromium (Cr-VI) are the most common forms and stable Cr species found in water (Chow et al. 2018; Salman and Elnazer 2020). However, as they are released into the environment, Cr(III) is metabolized to a poisonous hexavalent form that exists as Cr(VI) due to unstable environmental conditions (Balan, Shivakumar, and Kumar 2012). Cr-III is an essential component of human metabolism and is often used in vitamin supplements. Due to the adsorption of Cr on soil particles and the formation of insoluble complexes with functional groups and hydroxides, cationic Cr(III) is immobile in most soil conditions (Puls et al. 1994). On the other hand, anionic Cr(VI) attaches to soil colloids less firmly and thus has greater mobility (Shi et al. 2020). While Cr(VI) will reduce into Cr(III) in the presence of Fe(II), Fe(O), likewise several organic compounds and microorganisms can involve in the reduction process (Beukes et al. 2017).

The concentrations of chromium (Cr) in polluted soils in the Vellore District are incredibly high, meaning that the tannery industry soils are highly contaminated. For example, in many tanneries existing studies, Mahimairaja (2000) reported a massive Cr range (16731–79865 mg/kg) in subsurface soils. Rao, Rao, and Ranganathan (2013) have also reported a high TDS, Cr, and Fe concentration in groundwater due to sewage and tannery waste around the Ranipet area, Vellore District. In addition, chromium accumulation was reported higher in the sediments than water because of tannery effluent and natural sources near Ambur, Vaniambadi, Perambur, Ranipet, and Walajapet (Balaji et al. 2015; Sundar and Chandrasekaran 2010).

In this current research study, the evaluation of chromium contamination of soils around the new tannery industrial area of Vellore district, located in Southern India, has been targeted. The major towns of Vellore district viz. Vaniyambadi, Walajapet, Gudiyatham, Thirupattur, Arcot, and Vellore have been chosen to evaluate and specify heavy metals in the soil and their distribution in the surface soils. Furthermore, no comprehensive study has been done in these regions that have determined the effect of Chromium (III) and (VI) separately on soil pollution. Therefore, the present study also aims to assess the impact of Chromium (III) and (VI) and quantify the contamination of major ions and trace elements in the agricultural soils around tanning industries using statistical and EBK modeling techniques.

Materials and methods

Research area description

The research area is situated in southwestern parts of the Vellore District of Tamil Nadu, covering around 781 sq. km (Figure 1). The temperature ranges from 18.2 to 36.8°C, with the hottest months being May and June. These regions lie in a part of the Palar river basin, and the drainage pattern is dendritic to semi-dendritic in nature. Generally, the climatic condition of this area is arid to semi-arid. Hence, groundwater is used for drinking, domestic, industrial, and agricultural purposes. The lithology of this region consists of three rocks, namely, Archean crystalline rocks (granite, epidote, hornblende gneiss), sedimentary rock (90%), and hard rock (10%). In addition, hornblende, Muscovite, Pyroxene, Plagioclase, Quartz, Microcline, and Biotite have been observed in the region (Figure 2).

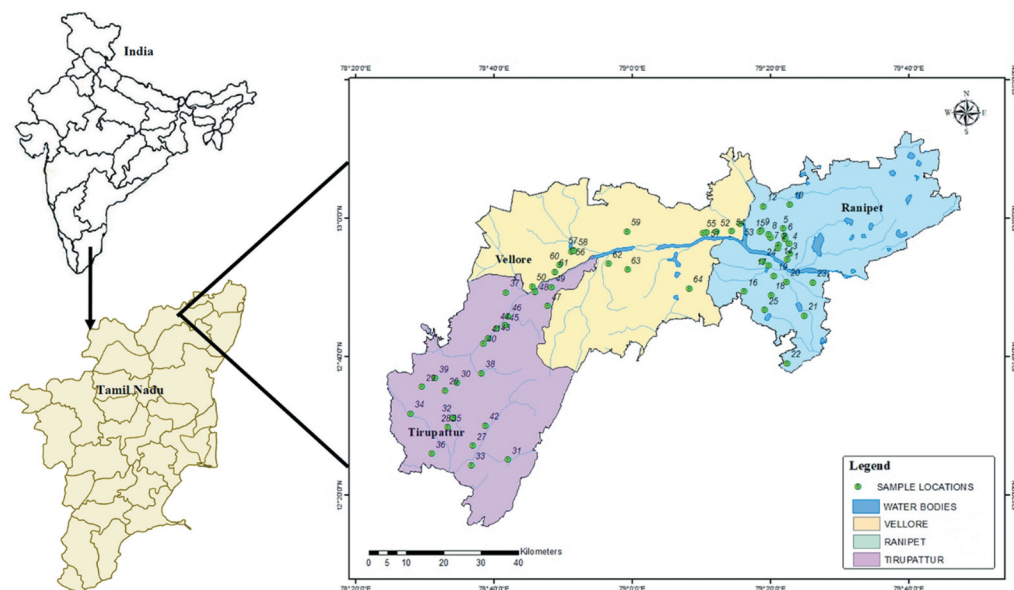


Figure 1. Location map of the study area and sampling site.

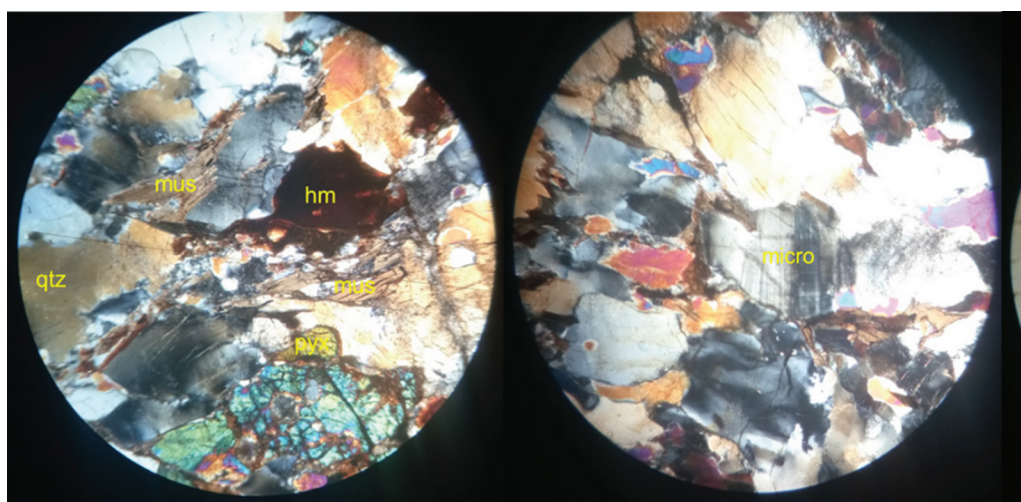


Figure 2. Identify the minerals based on the thin section in the study area (mus- Muscovite; qtz-Quartz; hm-Heavy mineral; horn-Hornblende; pyx-Pyroxene; bio-Biotite; fel-Feldspar; or-Orthoclase; plag-Plagioclase; micro-Microcline).

The study area has large tannery units located in and around the town. In addition, other industries like ceramic, refractory, and chromium production also function on a small scale. The tannery industries use several chemicals such as sodium sulfate, sodium carbonate, fat liquors, chrome sulfate, vegetable oil, and dyes during leather processing. In the Ranipet region, the tannery industrial effluents are discharged into

Puliathengal, Vanapadi, and Thandalam lakes, thus polluting the Palar River and causing ecological degradation and health hazards (Gowd and Govil 2008; Thangarajan 1999).

Material and analytical techniques

Sixty-four Surface soil samples were taken from agricultural lands near tanneries in villages across six taluks, including Arcot, Walajapet, Thirupattur, Gudiyatham, Vaniyambadi, and Vellore. Before the collection of samples, the sampling location was fixed based on a grid pattern. Then, according to the soil degradation map of chromium (Natarajan et al. 2009; Rangasamy et al. 2015), the site was fixed, and the samples were collected from nearby tannery industries having proximity to the agricultural fields. Global Positioning System (GPS) was used to fix the geographic coordinates from each sampling station. ArcGIS 10.3 software was used to plot the sampling stations using their respective geographic coordinates. The locations of the soil sampling sites are shown in Figure 1. Surface soils were collected at a 5–10 cm depth from nearby agricultural lands around the tannery region.

The samples were digested using aquaregia comprising 1 part of HNO_3 and 3 parts HCl until the dense white fumes began to emerge. After cooling, 20 mL of distilled water was added to the samples and boiled till white fumes disappeared. Whatman 42 filter paper was used to filter each sample. Generic methods were used to test the samples for chemical constituents (USEPA 1979). Using a Spectrophotometer instrument, the hexavalent Cr was calculated using the diphenyl carbohydrazide spectrophotometer system (ASTM 2002). The Cr (III) can be determined using the equation below (Salman and Elnazer 2020; Zhao et al. 2019)

$$\text{Cr(III)} = \text{total Cr} - \text{Cr(VI)} \quad (1)$$

The trace elements and total Cr present in the solution was calculated by Atomic absorption spectrophotometer (Varian Spectra AA220) using air acetylene flame at 357.9 nm (USEPA 1993). The trace elements of surface sediment samples were determined in the soil testing laboratory of the National Agro Foundation, Chennai using advanced techniques and standard procedures adopted from the USEPA (1979). Merck CRM standards were used to prepare the calibration curve for each element. Seven trace metals like Cr, Fe, Cu, Mn, Pb, Zn, and Ni were analyzed. For multivariate statistical analysis such as correlation matrix and factor analysis, IBM (SPSS) version 20.0 software was used. EBK geostatistical modeling and generation of semivariograms were done with the help of ArcGIS10.3 software. The Pollution Index (PI) was estimated using the following equations (Nishida and Hiraiwa 1982).

$$PI = \left[\left(\frac{Cu}{100} \right) + \left(\frac{Pb}{100} \right) + \left(\frac{Fe}{5} \right) + \left(\frac{Zn}{300} \right) + \left(\frac{Ni}{50} \right) + \left(\frac{Cr}{100} \right) + \left(\frac{Mn}{5000} \right) \right] / 7 \quad (2)$$

Geoaccumulation Index (GI) was calculated by the following equation (Muller 1969; Shacklette and Boerngen 1984)

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n} \right] \quad (3)$$

C_n – concentration of elements

B_n – concentration in the Earth's crust of the element average

Geostatistical modeling

The spatial distribution of major and trace elements in the surface soil samples was assessed using the Empirical Bayesian Kriging (EBK) interpolation modeling method. The sample locations were used to interpolate the surrounding values, and these values were derived based on deterministic model distributed values (Krivoruchko, Gribov, and Krause 2011). The collected sampling point and related uncertainty with the interpolated standards were derived based on predictor model values. All of the studied parameters were calculated using this method for sub-setting and simulating the observed data.

The classic Kriging model frequently uses a single semivariogram model. However, EBK proposes several semivariogram models that account for semivariogram estimation uncertainty. It also processes the distribution of semivariogram, transformation, normal error prediction error, and standard error from the original dataset. The significant advantage of the EBK model is to approximate the presented error from the semivariogram. Typically, the EBK model calculates the value based on the following three significant steps: (1) The original observed data is used to forecast the semivariogram model (2) new values derived from the original data are used to construct a new semivariogram model, and (3) new simulated data is produced using the new semivariogram model. The unsampled coordinates of the new semivariogram model's envisioned weights were predicted using standard errors determined using the K-Bessel style semivariogram with an analytical integration, which is the most compact and reliable approach but takes the longest to process. Four types of errors are used in the EBK model of estimation errors: mean standardized, root-mean-square, root-mean-square standard error, and average standard error. The root-mean-square standard error values should be similar to the average standard error values. The EBK modeling techniques are crucial to yield an appropriate spatial distribution model for the trace elements.

Results and discussion

Physicochemical characteristics

Surface soil samples were analyzed for physico-chemical parameters and trace elements, and the results are shown in Table 1. According to the findings, soil pH ranged from 7.4 to 8.4, with an average value of 7.9, signifying alkalinity in the study region. Generally, when pH increases above 7.4, the oxidation of ammonia to produce nitrate or the oxidation of sulfur to produce sulfate was mediated by bacterial activity. In addition, oxidation of Cr(III) in MnO_2 has been reported (Johnson and Xyla 1991; Shams et al. 2009). The Thirupathur region had the lowest pH (7.4), and the Arcot region had the highest pH (8.4). About 70% of samples had a pH of more than 8.5, indicating sodicity in soil. In the case of low acidity, more chromium was leached with acidic rainwater as chromium appears only as soluble Cr(III) species in the acid pH ranges (Wolf et al. 2011), produced by the reduction of Cr(VI) (Nouri et al. 2017). A higher concentration of pH value was found in the southern part of the study area (Figure 3a).

The electrical conductivity (EC) in the soil samples ranged between 0.1 and 2.2 dS m^{-1} with an average of 0.6 dS m^{-1} . The spatial distribution indicates a high concentration of EC was lying in the northern part of the region (Figure 3b). Due to tannery effluent and geochemical processes, the soil samples near the tannery and rock

Table 1. Minimum, maximum, and average values of measured geochemical parameters of the Soil.

Parameters	Minimum	Maximum	Average
pH	6.6	8.7	7.8
EC (dS m ⁻¹)	0.1	2.2	0.6
OM (mg/kg)	0.3	2.7	1.4
P (mg/kg)	1.0	135.9	22.3
Ca (mg/kg)	444	5973	2858
Na (mg/kg)	22.3	1140	438.6
K (mg/kg)	10	327	123.4
Mg (mg/kg)	186	1531	761
Cr (mg/kg)	1.0	751	53.6
Pb (mg/kg)	1.4	72.7	21.1
Ni (mg/kg)	0.0	107.5	22.5
Mn (mg/kg)	0.6	25.1	5.4
Fe (mg/kg)	2.6	118.2	18.5
Zn (mg/kg)	0.2	5.6	1.3

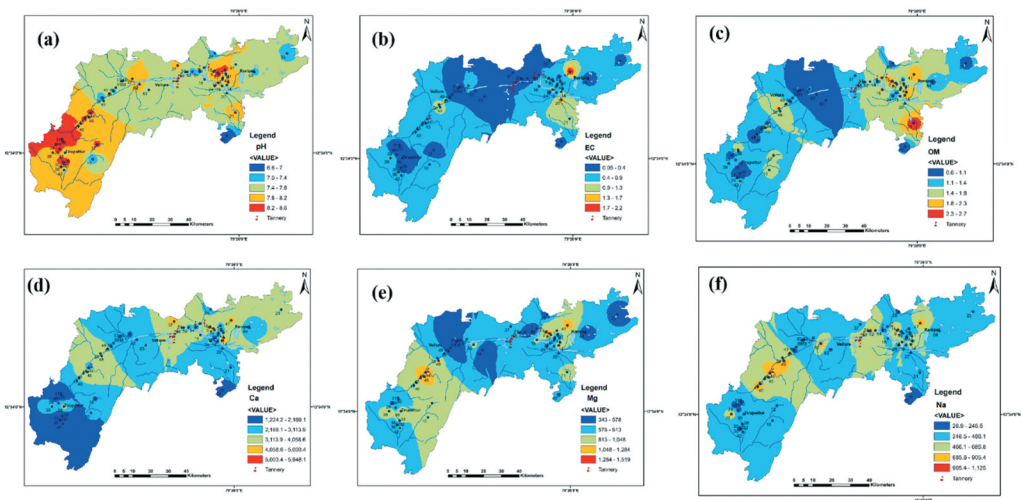


Figure 3. Spatial variation of the (a) pH, (b) EC, (c) OM, (d) Ca, (e) Mg, and (f) Na in the study area.

weathered region had a higher pH and EC value. In the study area, the Organic Matter content (%) of the samples ranged between 0.3 and 2.7 with an average of 1.4. A high content of organic matter (OM) of the samples was found in the eastern and northern regions (Figure 3c).

Calcium (Ca) variability in the soil samples ranged between 444 and 5973 mg/kg with an average of 2858 mg/kg. The southern and central parts of the region were noticed with high Ca content than the other region (Figure 3d). Magnesium (Mg) concentration in the soil samples was speckled from 186 to 1531 mg/kg with an average of 761 mg/kg (Figure 3e). Analytical results of sodium (Na) in the samples have ranged from 22 to 1140 mg/kg within a mean value of 438.6 mg/kg (Figure 3f). Sodium carbonate and sodium sulfate dyes are commonly used in the tannery industries during the leather processing process. The potassium content of the soil samples ranged between 10 and 327 mg/kg with an average of 123 mg/kg. The spatial distribution indicates the higher potassium concentration in the soil sample, close to the agricultural and tannery region.

Trace elements and chromium (III) and (VI).

The analytical result of the trace element concentrations in the soil samples followed the decreasing order $\text{Cr} > \text{Fe} > \text{Ni} > \text{Pb} > \text{Mn} > \text{Cu} > \text{Zn}$, and the values are shown in Table 1. The high concentration of Cr in the soil is because of the direct disposal of effluents from the tanneries (Tarcan, Akıncı, and Danışman 2010). The Cr variability in the soil samples ranged between 0.1 and 2459 mg/kg with an average of 53.6 mg/kg. The northern and central parts of the region were noticed with high Cr content in the soil compared to the other region (Figure 4a). The results indicate that among the various industries in vellore, tannery industries are major producers of heavy metals like chromium, manganese, copper, lead, cadmium, and nickel (Uddin and Ahmed 2018). Higher content of Cr was detected near the study area due to the influence of tannery effluent because the effluent released on land particularly at high concentration (100%) increased chromium content in soil (Prasad et al. 2021). Pb content in the soil samples was ranged from 1.4 to 72 mg/kg; a high concentration of Pb was noticed in the northern and central parts of the study area (Figure 4b).

Generally, the content of OM and pH increases with Ni adsorption (Sathya and Mahimairaja 2015a, 2015b). The Ni content in the soil samples ranged between 0.001 and 107 mg/kg. The northern and central part shows high Ni concentration due to tannery effluents and geogenic activities. Commonly, MnO is used in leather production in chromium tannery industries (Tariq et al. 2010). Therefore, Mn is a vital factor found in various salts and minerals combined with Fe compounds. In the test area, the Mn content of the soil samples ranged from 0.06 to 25 mg/kg with an average of 5.4 mg/kg. Generally, the concentration of Fe in the soil depends on weathering from source rocks and the discharge of waste effluents.

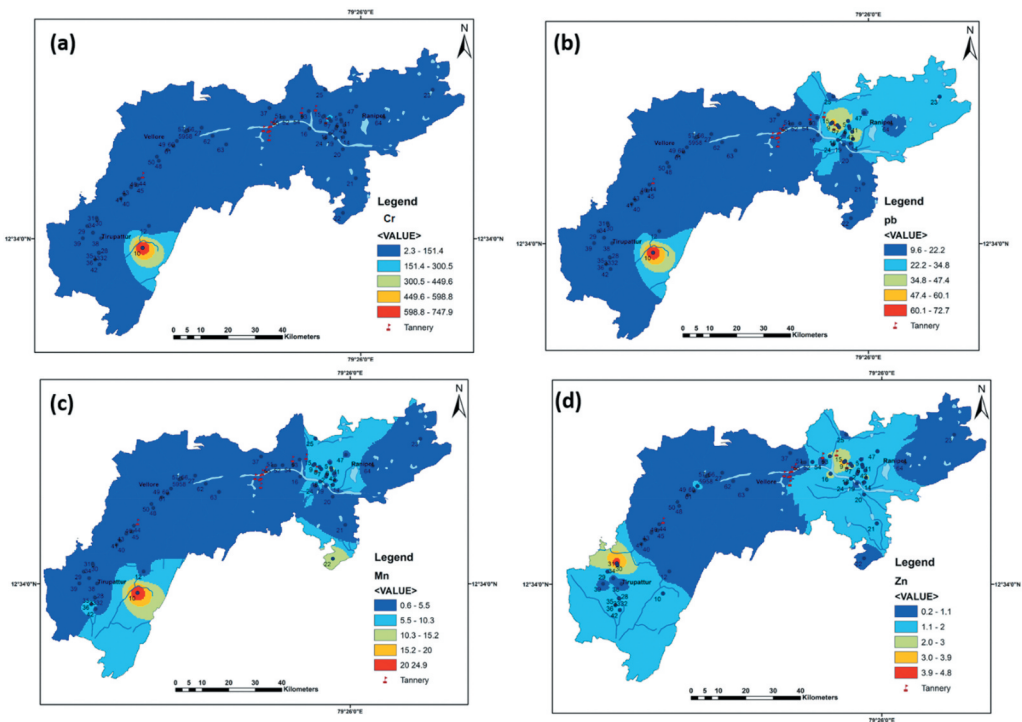


Figure 4. Spatial variation of the (a) Cr, (b) Pb, (c) Mn, and (d) Zn in the study area.

The Fe content lies between 2.6 and 118 mg/kg, an average of 18.5 mg/kg. The spatial distribution indicates that higher levels of Mn were observed in the eastern and central parts of the region (Figure 4c). In the study area, some of the locations show high content of Fe and Mn, which are related to the natural weathering of source rocks and anthropogenic activities. The concentration of Cu and Zn increases in the soil due to the return flow of agriculture and fertilizers seepage (Magesh, Chandrasekar, and Elango 2017). The concentration of Cu in the soil ranged from 0.2 to 10.6 mg/kg. The concentration of Zn in soil ranged from 0.2 to 5.6 mg/kg, with an average of 1.3 mg/kg in the region. In the study area, the content of Cu and Zn increased due to industrial effluents and agrochemicals like fertilizers and pesticides. The content of Cr(III) in the soil ranged between 0.01 and 1727 mg/kg. In the study area, Cr(VI) concentration ranged between 0.01 and 737 mg/kg. The spatial distribution map indicates the high content of Cr(III) and Cr(VI), which was dominant in the northern and central parts of the area (Figure 4d), which is due to the influence of tannery effluents.

Multivariate analysis for soil pollution

Multivariate statistical techniques such as bivariate correlations, factor, and cluster analysis were used for elucidating the correlation among major ions and trace elements in the soil. Pearson correlation coefficient methods have been used to comprehend the relationship between the variables and their influential factors (Table 2). Cr associated with Ca, Mg, P, Mn, Pb, K, and Fe signifies anthropogenic and agricultural activities (Barajas-Aceves, Corona-Hernández, and Rodríguez-Vázquez 2007; Rahaman et al. 2016). The positive correlation of Cr with Ca, Mg, P, and Mn implies tannery wastewater discharge into the open land, contaminating the study area’s soil.

Similarly, a positive correlation was observed for Pb with Ca, Mg, Mn, Cr, and Cu, indicating anthropogenic sources, particularly from the industrial effluents and geogenic sources from rock materials. That goes well with the previous literature (Dwivedi and Vankar 2014). Generally, the trace elements such as Zn, Ni, Mn, and Fe, originated from industrial effluents. Moreover, the concentration of Ni had correlated positively with OM, Ca, Mg, Na, Mn, and Cr, which specifies industrial effluents. A positive correlation between Mn and Fe was observed in the study area. The source of Fe and Mn are connected with the natural weathering of source rocks such as charnockite, granite, and fissile hornblende

Table 2. Correlation matrix of soil geochemistry parameters.

	pH	OM	Ca	K	Mg	Na	P	Fe	Mn	Cr	Cu	Ni	Pb	Zn
pH	1.000													
OM	.043	1.000												
Ca	−.042	.500	1.000											
K	−.207	.110	.078	1.000										
Mg	.418	.468	.505	−.092	1.000									
Na	.103	.353	.468	.162	.437	1.000								
P	−.018	.095	−.338	.207	−.046	−.237	1.000							
Fe	−.144	.206	−.139	−.050	.052	−.182	.402	1.000						
Mn	−.113	.094	−.164	−.075	.146	−.149	.231	.453	1.000					
Cr	−.101	.081	.134	−.130	.290	−.011	.087	.022	.556	1.000				
Cu	.118	.562	.364	.134	.443	.288	.149	.317	.192	.183	1.000			
Ni	.211	.352	.404	−.194	.404	.213	−.009	.023	.251	.427	.370	1.000		
Pb	.167	.359	.322	−.270	.307	.072	−.034	.151	.476	.488	.502	.720	1.000	
Zn	.091	.448	−.060	.125	.089	−.094	.455	.331	.191	.043	.484	.056	.167	1.000

biotite gneiss, and it is also related to anthropogenic activities. However, since deep soil sediment has high ionic activities, it is linked to the release of Fe in the soil system. Cu shows a positive correlation with K indicating agricultural return flow and seepage of fertilizers in the study area.

Principal component analysis (PCA) and hierarchical cluster analysis (HCA) are two popular methods for determining the relationship between two or more components and the source of contamination. The analytical result of the major ions and trace elements in the soil samples have been grouped into four Principal components (PCs) (Table 3). The PCA loading of three major components is shown in (Figure 5). The high variance of elements was loaded in PC1 (21.8%), which corresponds to OM, Mg, Cr, Cu, Ni, and Pb, representing the anthropogenic source of contamination from tannery effluents. The second component (PC2) is accountable for 18.2% of the total variance and shows moderate loadings for metals such as Fe, Mn, Cr, and Zn.

Table 3. Component matrix of soil geochemistry parameters.

Parameters	Components			
	1	2	3	4
pH	0.221	−0.215	−0.066	0.857
OM	0.709	−0.055	0.441	−0.043
Ca	0.564	−0.581	0.145	−0.299
K	−0.077	0.027	0.632	−0.420
Mg	0.702	−0.300	0.045	0.226
Na	0.384	−0.585	0.291	−0.136
P	0.080	0.703	0.306	0.139
Fe	0.259	0.663	0.154	−0.007
Mn	0.414	0.600	−0.381	−0.226
Cr	0.494	0.211	−0.521	−0.330
Cu	0.755	0.110	0.348	0.023
Ni	0.731	−0.111	−0.344	0.023
Pb	0.767	0.097	−0.410	−0.007
Zn	0.379	0.514	0.475	0.235

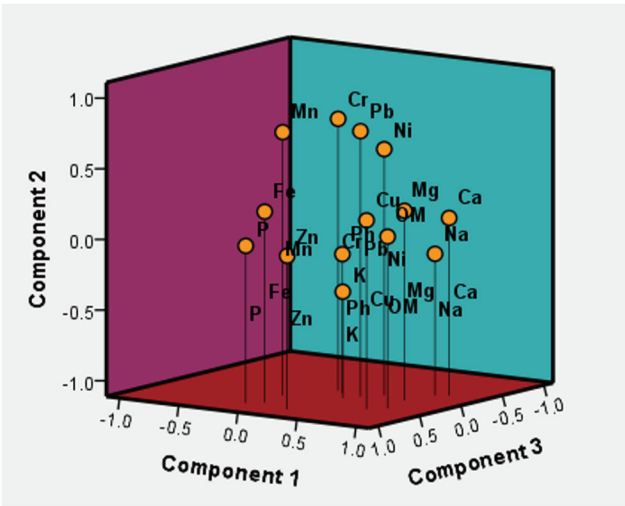


Figure 5. 3D Principal component in the study area.

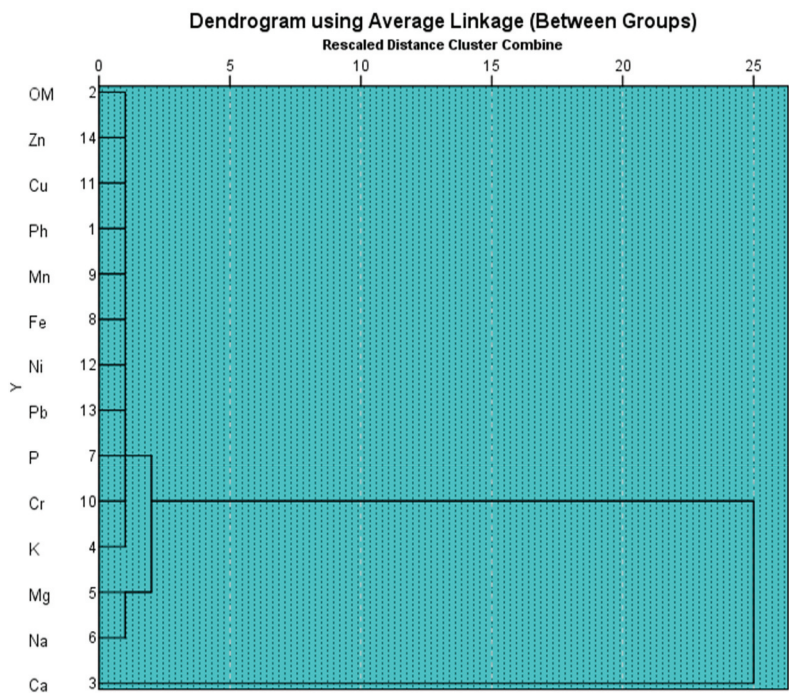


Figure 6. Hierarchical Cluster Analysis in the study area.

PC2 indicates the dominance of Fe and Mn in the soil samples associated with the chemical composition of rock materials through natural weathering. PC3 represents 17.0% with metals such as K, Fe, Cu, Pb, and Zn, which may have originated from fertilizers through agriculture activities and seepage of industrial effluents in the study area. Hierarchical Cluster Analysis (HCA) for the major ions and trace elements in the soils show two different clusters in the study area (Figure 6). The first group of clusters epitomizes the sample locations, which groups the anthropogenic activities and lithological influences. Moreover, the result highlights that tannery effluents and natural weathering sources control elemental contamination.

Geostatistical modeling for soil pollution

For all of the important trace elements and ions in the research area, the EBK modeling results made it possible to accurately predict errors that yielded the mean normalized, root-mean-square, root-mean-square standard error, and average standard error. Generally, the root-mean-square and average standard error values should be very close, and also, the root-mean-square standardized value equal to one indicates the best modeling. Sometimes, root-mean-square standardized value shows the values above or below one. This specifies overestimation and underestimation of prediction variability, respectively. The model implementation and the predicted graph for the selected parameters such as Cr, Pb, Fe, and Ni were assessed. The root-mean-square standardized for the study, yielded the following results for the soil samples observed in the region: pH (0.95), EC(1.0), OM (0.96); Major Ions (Ca

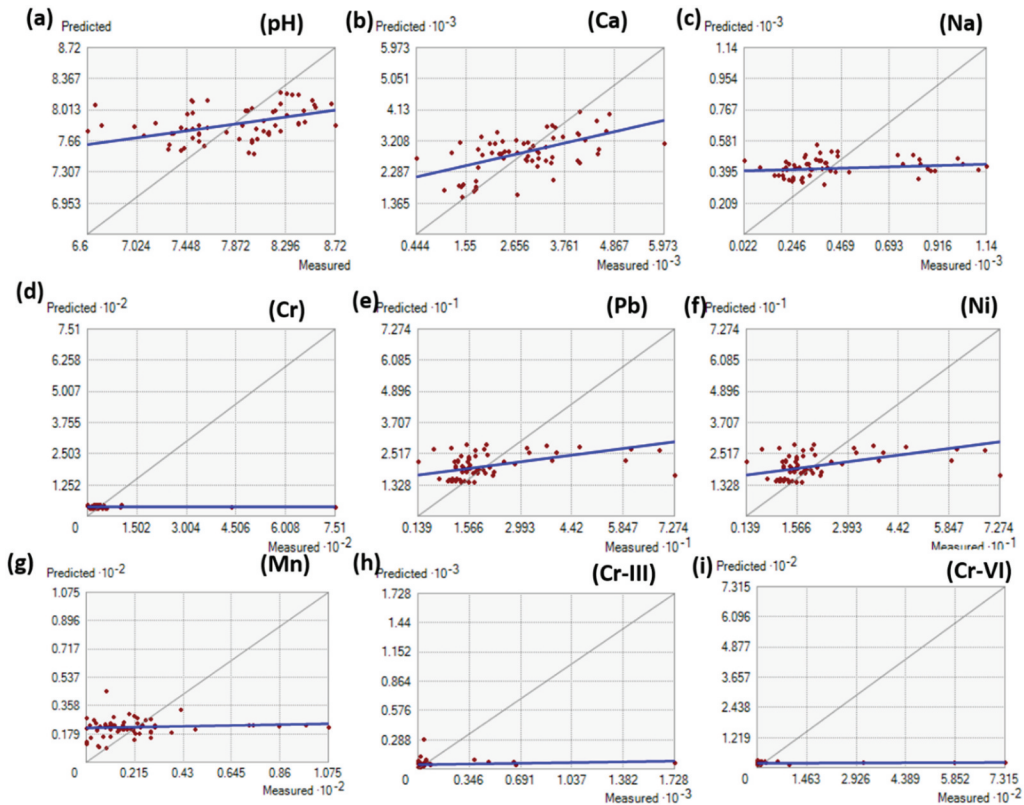


Figure 7. (a-i) Empirical Bayesian Kriging (EBK) modeling result of prediction errors in the study area.

(0.95), Mg (0.96), Na (1.02), K (0.97) and trace elements (Cr (1.8), Pb (0.93), Ni (0.98), Cr (III) (2.0) and Cr(VI) (2.2)). These values are close to one (1), indicating valid prediction (Figure 7).

Furthermore, semivariogram models of the studied parameters are shown in Figure 8, where the x and y-axis indicate distance in meters. Semivariogram considers multiple plots, such as the color of the blue line, which indicates semivariogram distribution. In contrast, the blue line part shows an additional semivariogram. However, the Solid red line indicates the median of the spreading surrounded by red dotted lines. Blue cross lines in the semivariogram spectrum, roughly in the middle, mark the highest empirical semivariance. The soil's high pH, Ca, Na, and K content was recorded in the southern and northern parts compared to the other region (Figure 9). The high content of Cr was recorded in the south and north parts of the region (Figure 10). Tannery effluents cause high Cr in the study area because the tannery industries use chemicals for leather processing. A high concentration of Pb was observed in the southern and northern parts of the study area (Figure 10). Other trace elements show a similar pattern as Pb in the soils. The south and central parts of the study area show high content of Ni derived from natural weathering of source rocks such as granite, charnockite, hornblende gneiss, epidote, fissile hornblende biotite gneiss, or aquifer material, and it is also related to anthropogenic activities.

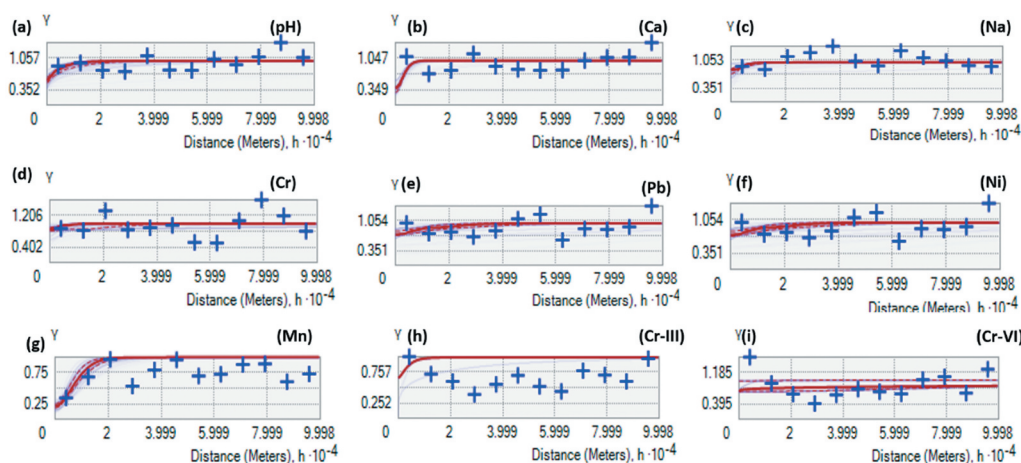


Figure 8. (a-i) Semivariogram graph of the trace elements derived from Empirical Bayesian Kriging (EBK) modeling.

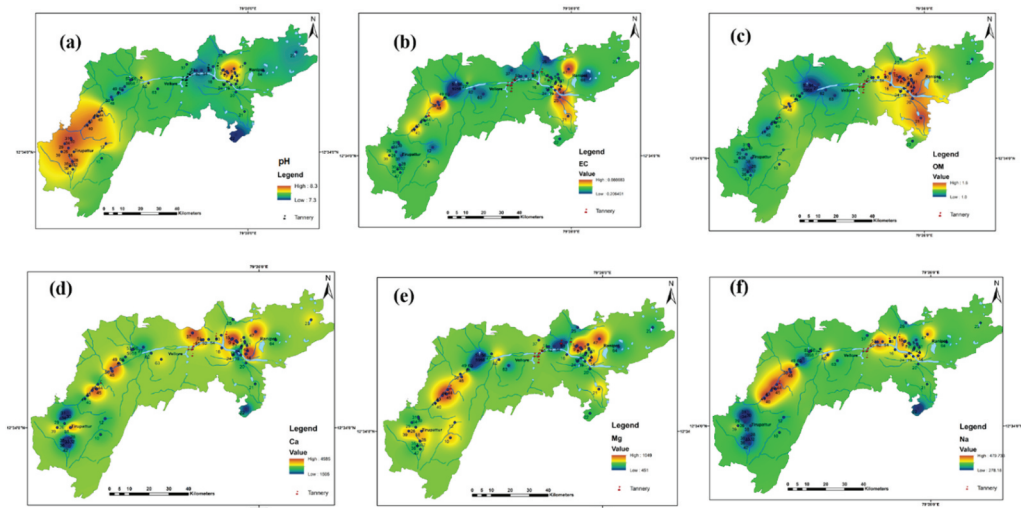


Figure 9. Spatial distribution of the results (Major Ions) of Empirical Bayesian Kriging (EBK) modeling.

Pollution Index (PI) and Geoaccumulation Index (GI)

Pollution index (PI) is the assessable estimation of the gradation of tannery effluent mixing in the local soil sediments. The pollution index (PI) suggested by Nishida and Hiraiwa (1982) is used to describe the possible source of contamination in the soil of the test area. Many researchers have studied the distribution of soil sediments based on the PI values (Tarcın, Akıncı, and Danişman 2010). The concentration of elements of the PI values of the soil, when above 1.0, indicates the impact of anthropogenic activities (Tarcın, Akıncı, and Danişman 2010). Acceptable level values for Mn, Zn, Ni, Cr, Cu, Pb, and Fe are obtained from Gemici (2008) for other elements. PI was calculated by following the above equation (2) based on the content of seven elements.

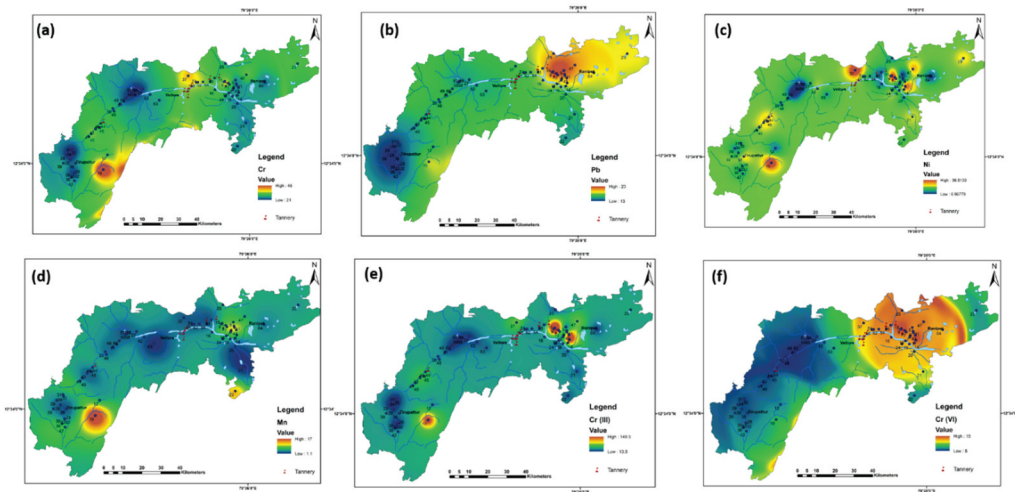


Figure 10. Spatial distribution of the results (Trace elements) of Empirical Bayesian Kriging (EBK) modeling.

The concentration of PI values of the soil samples ranged from 0.1 to 3.4 were observed in the study area. Location 3, 6, 8, 9, 10, 11, 16, 22, 30, 31, and 35 of the soil samples have PI values above (1.0) as these locations were present near the tannery region, indicating the anthropogenic impact. Particularly in samples 6, 10, 11, and 22, a high impact of tannery effluents was observed. Geoaccumulation Index is another factor to consider when assessing pollutants in soils (GI). According to the Geoaccumulation Index, soil sediments can be classified into five categories: (1) uncontaminated to slightly polluted, (2) moderately contaminated, (3) moderately to heavily contaminated, (4) 3–4 heavily contaminated, (5) heavily to significantly polluted, and (6) >5 extremely contaminated suggested by (Loska, Wiechuła, and Korus 2004; Muller 1969; Tarcan, Akıncı, and Danişman 2010). Geoaccumulation Index is calculated by equation (3) (Loska, Wiechuła, and Korus 2004; Muller 1969; Tarcan, Akıncı, and Danişman 2010). Geoaccumulation Index (GI) was used to estimate the contamination of soil samples. Based on this classification, most of the samples fall under the uncontaminated to moderately contaminated category. Few of the samples fall under the moderately to heavily contaminated category. Moreover, PI and GI results of the samples around the tannery region also show the heavy impact of tannery effluents.

Evaluation of heavy metals

The soil quality was assessed based on the permissible limits for the selected parameters such as Cr, Pb, Mn, Ni, Zn, Cr(III), and Cr(VI). The high concentration of Pb, Mn, Ni, Zn, Cr(III), and Cr(VI) was observed in the northern and central parts of the area (Figure 11). The high content of trace elements in the soil samples was observed in the Walajapet block. These samples were taken from areas near tannery industries that tannery effluents could have harmed. The tannery industries use various chemicals and salts for leather production. The industrial effluents dumped in open land have an impact on both the environment and human health. Toxic heavy metals have severe

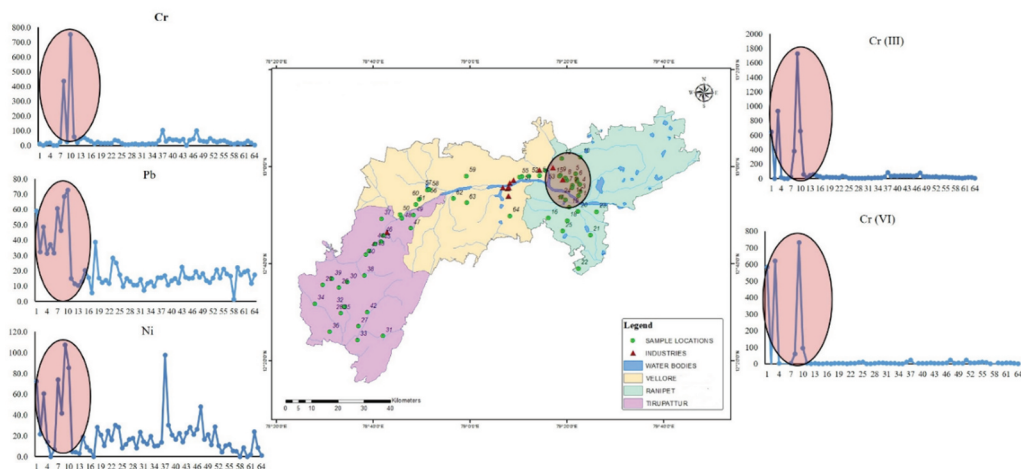


Figure 11. Evaluation of soil quality based on the selected parameters Cr, Pb, Ni, Cr (III), and Cr (VI).

deteriorating effects on several microorganisms, plants, and animals (Rahman and Singh 2019). Trace elements such as Pb, Mn, Ni, Zn, Cr(III), and Cr(VI) have also been accumulated in the soil of this area.

Moreover, vegetables and other food products may accumulate these trace elements and end up in the human body through the food chain. The high concentration of Cr in the tannery surrounding area topsoil samples might be due to industrial wastes such as Cr pigment, raw tannery wastes, and leather industrialized wastes. Cr pollution in the topsoil might be due to waste consisting of Lead-Chromium batteries, surplus plastic materials, and unfilled paint containers (Kistan et al. 2018). The high concentrations of Cr, Pb, and Zn in the soil are hazardous to human health, causing blood pressure, kidney damage, miscarriages, brain injury, skin rashes, stomach upset, ulcers and lung cancer, etc. In the study area, a few locations have a high content of Fe and Mn, which are associated with the natural weathering of source rocks (charnockite, granite, epidote, hornblende gneiss, fissile hornblende biotite gneiss) and anthropogenic activities. Therefore, as a first step in preventing pollution, hazards, and risks to soils, proper effluent collection and treatment systems must be installed in tannery areas.

Conclusions

The contamination of major ions and trace elements in soil samples, EBK modeling, and soil quality were assessed around the tannery industries of Vellore District. A positive correlation between Mn and Fe was observed in the study area. Normal weathering of source rocks such as granite, charnockite, epidote hornblende gneiss, fissile hornblende biotite gneiss, and anthropogenic activities has linked the source of Fe and Mn. Cu shows a positive correlation with EC indicating agricultural return flow and seepage of fertilizers. Particularly, samples 6, 10, 11, and 22 are highly affected due to the tannery effluents in the study area. Principal component analysis (PCA) indicates the dominance of Fe and Mn in the soil samples associated with the chemical composition of rock materials and natural weathering reactions followed by fertilizers from agriculture activities and

seepage dumped from industrial effluents. The EBK model highlights the high content of Na, K, Cr, Pb, and Ni around the tannery industries and agricultural areas. The high concentration of Pb, Mn, Ni, Zn, Cr(III), and Cr(VI) was noticed in the northern and central parts of the study area. The high content of metals in the soil samples collected near the tanneries in the Walajapet block indicates the impact of tannery effluents. Findings of results also confirmed that tannery effluents are seldom untreated and discharge improperly on land and waterbody that degrade the soil quality. Therefore, it is imperative to develop strategies to improve the functional efficiency of effluent treatment plants to prevent the improper discharge of untreated wastewater into the open drains and implement suitable remediation technologies for decontaminating chromium from agricultural lands and affected regions. Such remediation technologies would help keep agriculture afloat, but they will also help mitigate negative environmental consequences.

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No potential conflict of interest was reported by the author(s).

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Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article

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